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BIAS DUE TO SAMPLING GROUNDWATER AND SURFACE WATER FOR TRACE ORGANIC CONTAMINANTS

MOE Research Project # 449G

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Final Report

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PART 1. LOSSES DUE TO VOLATILIZATION

INTRODUCTION

Contamination of surface and groundwater by synthetic organic compounds is a major environmental concern in Ontario and most industrialized areas. In sampling natural waters for organic contaminants, two main sources of negative bias are recognized, loss of volatile compounds by partitioning into the atmosphere and loss of hydrophobic compounds by sorption onto synthetic polymers used in the construction of wells and samplers. Considerable research has been conducted at the Waterloo Centre for Groundwater Research and by numerous other research groups into the magnitude and the means to minimize these biases.

It is generally recognized that compounds with Henry's law constants greater than 0.001 (atm m^3 / mol) have the potential to be volatilized if the solution is exposed to the atmosphere during sampling and analysis. Most common organic groundwater contaminants fall into this category, and evaluating the potential for volatilization loss has been the object of several groundwater sampling studies. Barker and coworkers [1,2] evaluated the potential for volatilization and sorption losses when using multilevel piezometers and several other sampling devices. Ho [3] studied the effects of transport line material, pumping rate and sample lift height on the recovery of volatile organics in water with a peristaltic pump. Barcelona et al [4] tested a large number of samplers in an attempt to evaluate the effectiveness of various sampling mechanisms. Pearsall and Eckhardt [5] evaluated several common samplers and the effects of variations in sampling procedures and details of set-up. These studies have demonstrated that: 1) the potential for significant negative biases exists with common sampling devices, 2) the biases appear to be caused by volatilization (and by sorption in some cases), and 3) some consistency among studies has been found in the relative effectiveness of various samplers and sampling mechanisms.

Recently, particular emphasis has been placed on the problem of sampling gas-charged groundwater such as can be encountered in landfill leachate plumes and natural gas associated formations, for example. Pankow [6] provided a theoretical basis for estimating the artifacts due to bubble formation during sampling. Barker and Dickhout [2] tested the effectiveness of a positive displacement pump, an inertial lift pump and a peristaltic pump in sampling gas-charged water for volatile organics. Their finding that the peristaltic pump induced the greatest negative bias qualitatively agrees with theory; however, a consistent correlation between relative loss and Henry's constant was not observed, although only a narrow range of volatilities were represented by the compounds used.

It is evident that further research is required to realize the goal of quantitative estimation of sampling bias due to volatilization. The present study incorporates several improvements in design over the previous study by Barker and Dickhout [2]. Larger Henry's constant values are represented by the organic contaminants, and methane was included. Dissolved carbon dioxide concentrations were measured in order to establish a link with theory. In addition, the experimental well was constructed of stainless steel instead of PVC, eliminating the possibility sorption losses in the well; the well contained a sampling port at the bottom for obtaining representative control samples. Finally, six samplers were evaluated at two concentration levels, making this a more comprehensive study.

METHODS

An artificial well was installed in a stairway at the Waterloo Centre for Groundwater Research. The well essentially consisted of a 6 " diameter stainless steel pipe, 32' in height with a sampling port located near the bottom. The well was filled and drained at the bottom with an air-driven pump connected to a stainless steel reservoir. Gas-laden artificial groundwater, approximating that in an aquifer contaminated by low-level organics, was made as follows. A 90 litre volume of tap water containing 3.4 g/L sodium bicarbonate was prepared in the reservoir and its pH was adjusted to 9.0 with 1 N NaOH. The water in the reservoir was spiked with: 1) a saturated solution of methane in water, and 2) a methanolic stock solution containing benzene (366.5 mg/L), toluene (723.3 mg/L), trichloroethene (610.7 mg/L), trans-1,2-dichloroethene (262.1 mg/L), and 1,1-dichloroethene (254.0 mg/L). The spiking volumes that were used in the experiments are given below.

Experiment	Conc. Level	Volume (mL) Methanolic Stock	Methane Water
1-2	high	9.00	4000
1-1	low	0.45	415
2-2	high	9.00	4000
2-1	low	0.45	415
3-2	high	9.00	4000
3-1	low	0.90	1000
4	high	9.00	4000

After stirring, the solution in the reservoir was pumped through a port in the bottom of the well along with 2 L of a 10 % HCl solution, thus converting the bicarbonate ions to carbon dioxide. Since the bicarbonate and HCl solutions were proportionally mixed as they entered the bottom of the well, some of the carbon dioxide was liberated, but most was kept in solution by hydrostatic pressure in the well.

The following sampling systems were evaluated: a double check-valve stainless steel bailer (BAIL), a peristaltic pump (PER), a WaTerra inertial pump (WAT), an IEA syringe sampler (SYR), a Well Wizard bladder pump (WIZ), and a Solinst double-valve purge/sample pump (SOL). In each experiment, the high capacity foot-valve WaTerra (model D-32) and one or two other samplers were tested, and the water was sampled using the control port at the bottom of the well. In experiment 4, the high capacity WaTerra was compared with the smaller WaTerra (model D-16). Approximately the same well depth was sampled by all of the samplers. Five replicate samples were taken with each sampler and from the control port. Upon collecting a sample, two 60 mL hypovials were immediately filled to overflowing and capped with teflon-faced septa. The hypovials were stored underwater at approximately 4 C and the contents were analyzed within five days. The organic contaminants (benzene, toluene, TCE, 1,2-DCE, 1,1-DCE) were determined using one of the hypovials from each pair, and the other was used for determining the methane and carbon dioxide concentrations. The organic contaminants were determined in the headspace created in the hypovials when 15 mL of of sample was replaced with an equal volume of laboratory air. After equilibration, the headspace was injected directly into a gas chromatograph fitted with a photoionization detector. Methane and carbon dioxide were also determined by static headspace

gas chromatography with FID and TCD detectors. The relative standard deviations for five replicate determinations of the gases and the organic contaminants ranged from 4 to 8 %.

RESULTS

The data are summarized by experiment in Table 1, which gives the average concentrations for each group of five replicate samples. Percentage losses were calculated from the data of Table 1 by the formula

$$Loss(i,j,k) = -100 \times (Sampler(i,j,k) - Control(i,j)) / Control(i,j)$$

Sampler (i,j,k) is the mean concentration for compound i, concentration level j, and sampler k. Similarly, Control(i,j) is the mean concentration for the appropriate control sample. The percentage losses have been analyzed by the box plot technique [7]. In making statistical comparisons, a significance level of 0.05 was used throughout. Figure 1 depicts the percentage losses obtained by one-way classification according to compound, sampler and concentration level. Significantly positive biases are notably absent in all three categories. The difference in bias between the high and the low concentration levels is barely significant, with the high concentration bias being about 6 % more negative than the low concentration bias. The percentage loss incurred at the low level is not significantly different from zero. The percentage of compound lost by volatilization should not be affected by the concentration of the compound [6].

Considering next the box plots for the organic compounds, methane shows the greatest median loss, and this is significantly greater than the medians for the other compounds. Methane also shows a significantly greater variance. The methane losses are significantly correlated with the CO_2 losses (Figure 2), which suggests that volatilization is responsible for the methane losses. The other compounds are not significantly correlated with CO_2, and this is consistent with the fact the Henry's constant for methane is larger than those for the other compounds. The Henry's constants (atm m^3 / mol) for the compounds are [6]: methane, 0.676; 1,1-dichloroethene, 0.19; t-1,2-dichloroethene, 0.067; trichloroethene, 0.0091; toluene, 0.0067; benzene, 0.0055. The order of increasing loss among the compounds approximately parallels the order of increasing Henry's constant. Most of the variability among compounds is due to the contrast between methane and the other compounds. The 95 % confidence intervals (indicated by parentheses in the box plots) for the other compounds overlap extensively; for three of the compounds, the median biases are not significantly different from zero.

The variability associated with sampler bias, expressed as the standard deviation of the medians, is 4.3 %. This is comparable to the analytical variability for replicate analyses of the same sample. The sampling losses increase in the order: BAIL, SOL, WIZ, SYR, PER, WAT. The 95 % confidence intervals overlap extensively, so the order is not well-defined. The losses for the SYR, PER and WAT samplers are significantly different from zero, while those for the BAIL, SOL and WIZ samplers are not significantly different from zero or from each other. The losses for the large and small WAT samplers are indistinguishable from each other and are significantly greater than those for the BAIL, SOL, WIZ, and SYR samplers.

Table 1. **Mean concentrations (N~5) for each experiment. Concentrations are given in 10^{-6} g/L except for CO_2 which is given in g/L.**

Expt.	Sampler	Compound						
		BEN	TOL	TCE	1,2-DCE	1,1-DCE	METH	CO_2
1-2	CONT	16.8	33.6	26.5	10.8	10.4	408	1.24
	WAT	16.3	31.2	24.0	10.0	9.6	260	0.96
	BAIL	16.0	31.8	25.2	10.5	10.5	292	1.10
	PER	15.8	29.6	23.1	10.1	9.1	153	1.05
1-2	CONT	0.93	1.84	1.39	0.48	0.35	36.5	1.11
	WAT	0.91	2.10	1.42	0.47	0.32	14.6	0.97
	BAIL	0.91	2.14	1.50	0.52	0.42	33.6	0.81
	PER	0.91	1.58	1.42	0.45	0.34	8.6	1.01
2-2	CONT	21.7	42.6	35.3	14.4	13.3	232	1.24
	WAT	19.1	35.3	27.0	11.5	8.8	152	1.06
	WIZ	21.1	39.9	33.1	13.6	11.7	215	1.30
2-1	CONT	1.1	2.13	1.95	0.63	0.45	32.5	1.43
	WAT	0.99	1.98	1.60	0.56	0.37	16.0	1.13
	WIZ	1.1	1.83	1.95	0.55	0.35	31.3	1.35
3-2	CONT	19.4	39.4	29.1	13.6	12.4	426	1.97
	WAT	18.7	33.5	24.6	10.8	9.6	198	1.51
	SOL	20.3	36.6	29.7	12.1	11.2	347	1.90
3-1	CONT	2.13	3.60	3.19	1.09	0.76	95.0	1.94
	WAT	2.14	3.96	2.97	1.11	0.82	38.9	1.19
	SOL	2.11	3.99	3.07	1.04	0.72	64.3	1.66
	SYR	2.0	3.2	3.0	0.92	0.46	86.8	1.96
4	CONT	21.3	38.7	36.3	13.1	11.0	382	1.96
	LG.WAT	20.5	30.2	27.4	10.6	8.85	247	1.59
	SM.WAT	22.7	32.5	30.2	12.0	9.54	248	1.76
	SYR	20.4	36.1	33.9	12.7	10.1	338	1.82

Figure 1. Box plots of percentage loss (N = 108).

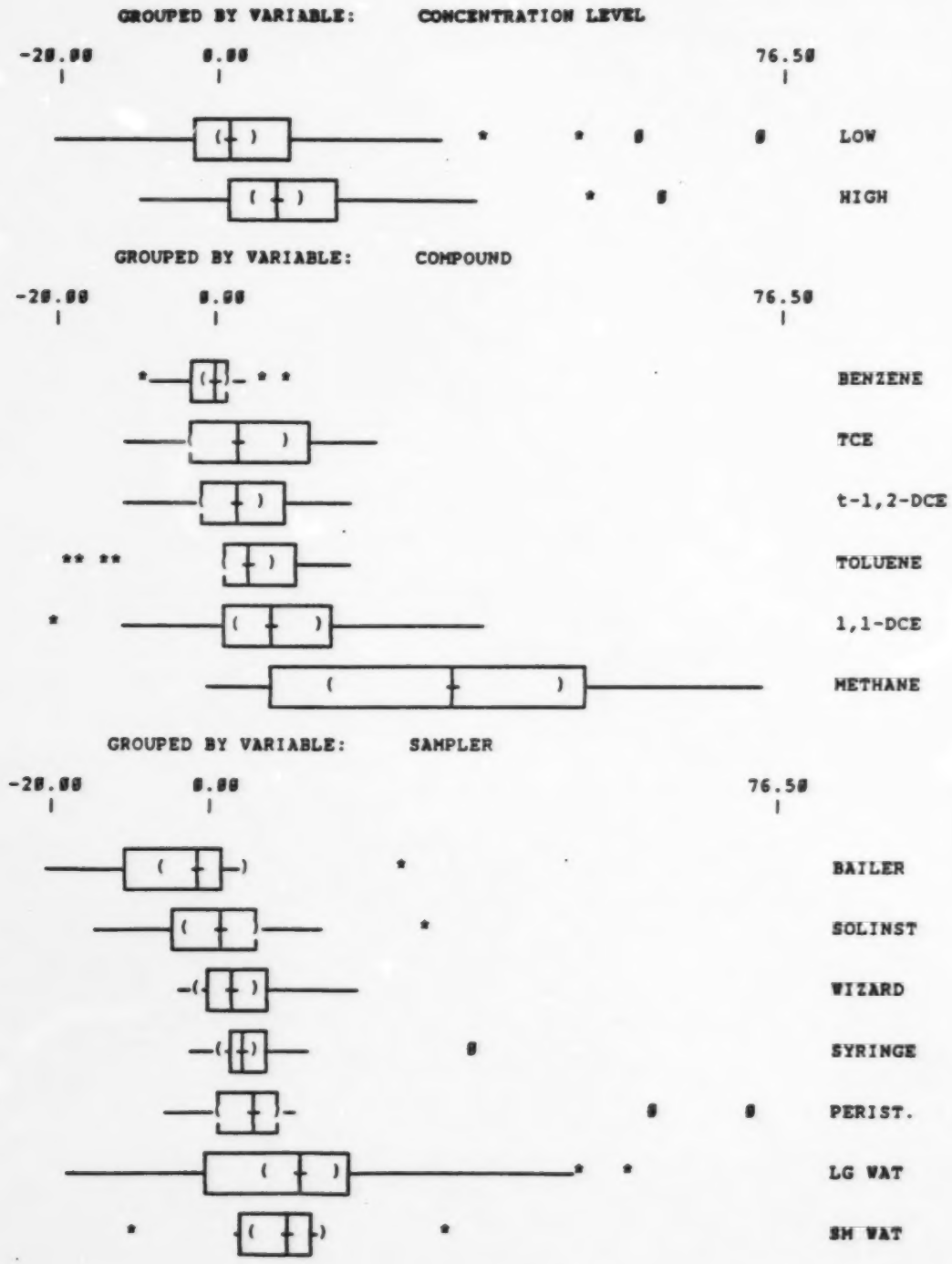
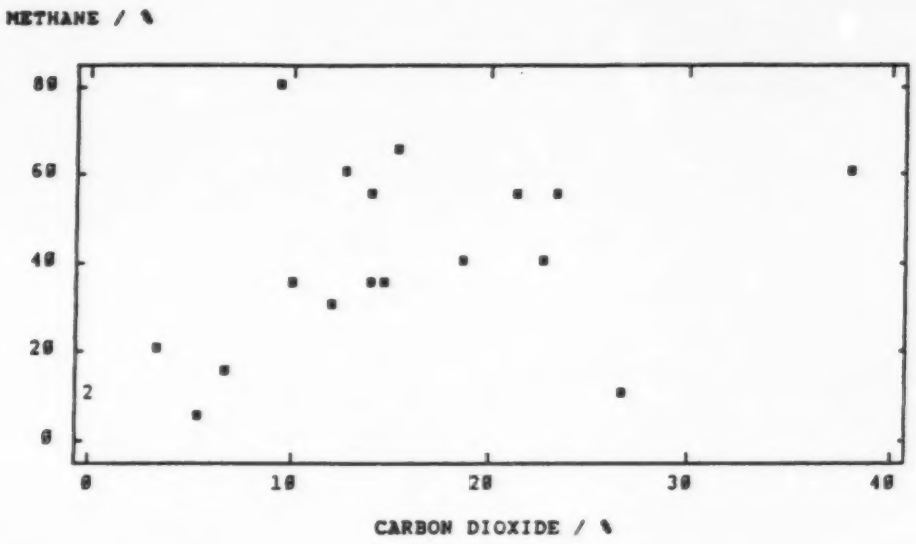


Figure 2. Scatterplot of percentage loss, methane versus carbon dioxide.



The box plots provide a robust (nonparametric) one-way analysis of variance. A two-way anova is more powerful, because the error mean square is reduced by taking into account the variance due to the other factor, but the experimental data violate the homogeneity of variance assumption. As mentioned previously, methane shows a larger variance. The simpler method of analysis (box plots) was used, because it is less prone to type II error (concluding that a significant difference exists when it does not). The methane data appear as outliers in the box plots for the samplers, thus exerting little influence on the medians and on the 95 % confidence intervals. This was verified by comparing the box plots in Figure 1 with those obtained when the methane data was deleted. The sampler losses depicted in Figure 1 are therefore representative for compounds having Henry's law constants smaller than 0.2 atm m^3/ mol.

The losses for methane indicate a somewhat different sequence for the samplers from that indicated by the other compounds. In order of increasing methane loss, the sampler sequence is SOL, SYR, BAIL, WIZ, WAT, PER. However, a one-way analysis of variance indicates that the sampler means are indistinguishable. Because the degrees of freedom for the test is small, it is not possible to discriminate small differences between sampler means for individual compounds. More replication would be necessary to test hypotheses concerning the relative effectiveness of the sampling devices for particular compounds. This provides some justification for pooling the compounds in the test for sampler effects, and further justification is provided by the fact that biases are not significantly correlated among the compounds, i.e. the assumption of independent errors is not violated.

The percentage losses computed from the data of Table 1 were also used to estimate the random variability associated with sampling. The sampling variability, expressed as a standard deviation, was computed for each compound by taking the square root of the mean square error of a one-way analysis of variance for sampler effects. The high and low concentration data

were pooled, yielding 12 degrees of freedom for the estimate. The variablitities for benzene and methane are 4 % and 33 %, respectively, and the middle compounds fall into the range of 11 to 17 %. The sampling variabilities tend to increase as the Henry's law constants increase. Because each datum is the mean of five replicate samples taken with a given sampler in a single day's experiment, the variability for single samples is greater. Assuming that the variability for samples taken on a single day is the same as that for samples taken on different days, the sampling variability for single samples is estimated to be in the range of 20 to 40 % for the middle compounds. Therefore, the systematic variability associated with the samplers (4.3 %) is small relative to the random variability associated with taking replicate samples with a given sampler. It is also worth noting that the sampling device may introduce less bias than the laboratory performing the analysis. This is demonstrated by the results of a recent interlaboratory comparison for the analysis of low molecular weight aromatic compounds, e.g. benzene, toluene, etc. (R. Dickhout, unpublished data). A relative standard deviation of 28 % was obtained for the 10 participating commercial laboratories, and this is considerably larger than the 4.3 % RSD obtained for the seven sampler medians.

DISCUSSION

The question of whether or not volatilization is the mechanism responsible for the observed losses of organic compounds can now be discussed. The fact that methane showed the greatest percentage losses is consistent with the relative magnitudes of the Henry's constants. Most of the variation in the biases for the compounds and in the Henry's constants is due to the contrast between methane and the other compounds. The fact that the methane losses are significantly correlated with the CO_2 losses (Table 1) strongly suggests that methane bias is due to volatilization. Recent sampling studies carried out in this laboratory (R. Dickhout, unpublished data), have revealed that substantial losses occur during the well filling procedure, apparently caused by the effervescesce produced when the sodium bicarbonate and HCl solutions are mixed.

Substantial amounts of carbon dioxide were lost during the sampling process. From the median percentage loss (15 %, Figure 2) and the typical concentration for CO_2 in the control samples (1 g/L, Table 1), it is estimated that about 0.07 mL of carbon dioxide gas was lost to the atmosphere per mL of solution. Pankow [6] has derived equations to predict sampling losses due to spontaneous bubble formation in gas-charged waters. Assuming that carbon dioxide gas bubbles were produced during sampling, Pankow's eq 11 predicts percentage losses ranging from 1.6 % for benzene to 86 % for methane. The predicted losses are, on average, about a factor of 2 greater than the observed percentage losses (Figure 1). However, gas stripping of volatile compounds is not likely to be the mechanism responsible for the observed losses. The estimated in situ gas pressure (fugacity) for dissolved carbon dioxide in the well is 0.68 atm. Spontaneous formation of gas bubbles cannot occur unless the ambient pressure is reduced to a value smaller than the in situ gas pressure plus the vapour pressure of water. The peristaltic pump is the only sampler which could cause a substantial reduction in the ambient pressure. It is therefore postulated that the volatile compounds were lost by mass transfer at the air-water interface. The lack of an exact correlation between percentage loss and Henry's constant value may be due to the possible non-equilibrium nature of the postulated mechanism or due to the fact that the losses were small relative to experimental error.

Because it is a gas at room temperature and pressure, methane has a much greater potential for volatilization than for sorption by synthetic polymers. The other compounds would have greater potential for sorption relative to methane because they are liquids. Interestingly, the order of increasing Henry's constant is similar to the order of decreasing solubility in water for the compounds. A compound's solubility in water is correlated with its polymer-water partion coefficient, so the tendency for sorption losses would be expected to approximately parallel that for volatilization losses among compounds having a narrow range of boiling temperature, which is the case for the liquids used in the experiments. Some of the samplers used in this study expose the sample to synthetic polymers. For example, plastic transfer line tubing was used with the WAT, WIZ, PER and SOL samplers. Exposure to polymeric materials is thought to be minimal for the BAIL and SYR samplers. The order of bias among the samplers does not appear to be correlated with the degree of exposure to organic polymers, however.

The relative performance of the samplers seems to be consistent with the results of previous studies [2,4,5] which show that sampler bias tends to increase in the order: grab samplers, positive displacements pumps, suction pumps (PER). The inertial lift pump (WAT) has not often been included in previous studies. The one published evaluation [2], indicated that the WAT sampler performed as well as the WIZ sampler and better than the peristaltic pump. In the present study, the WAT sampler did not perform as well as the other samplers. This apparent discrepancy may reflect differences in the way the samplers were used in the two studies, since it was previously shown [3,5] that factors such as rate of pumping and sample lift height can influence bias.

The present study has shown that the random variability associated with taking replicate samples is large relative to the variability associated with the different sampling devices. This means that large numbers of independent sampling events are needed to discriminate differences in sampler performance. The previous studies of sampler bias have not in general provided a firm statistical basis for discriminating differences in sampler performance, and the results of the present study are circumscribed by the kind and degree of replication employed and other details of the experimental design. The relative and absolute biases associated with sampling devices in such studies may be influenced by implicit conditions that will require considerably more effort to elucidate.

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PART II. LOSSES DUE TO SORPTION

INTRODUCTION

Synthetic polymers are almost ubiquitous in ground and surface water sampling equipment. They have the ability to sorb organic contaminants as evidenced by their use as chromatographic packings and as solid phase extractants. This suggest that a knowledge of the sorptive properties of synthetic polymers would be useful for the design and effective use of equipment for sampling organic contaminants.

Sorption of organic compounds by synthetic polymers has been thoroughly studied from the point of view of protection of water supplies (1) and for various other applications (2), but the implications for water sampling are not fully appreciated. Recently, we reported studies (3,4) in which sorption rate constants were measured for low molecular weight halogenated and aromatic hydrocarbons with a number of polymers. The mechanism of sorption was shown to be diffusion in the matrix of the polymer. The halocarbons were also depleted by three metals, including stainless steel, and it was thought that reductive hydrogenolysis reactions were responsible. It was observed that the sorption rates were dependent on the flexibility of the polymer, the water solubility of the compound, the contact area and the temperature, but that the rates were independent of solution concentration. A mathematical model was applied to explain the concentration histories observed in the batch sorption experiments and thereby obtain values for the sorption rate constant, K^2D, for each polymer-compound combination. Here K (dimensionless) is the polymer-water partition coefficient and D (cm^2/s) is the diffusivity of the compound in the polymer. It was possible to obtain the values of K and D separately for polyethylene, and these were found to be consistent with literature data. The studies demonstrate that synthetic polymers have the potential to cause sampling bias for these common organic contaminants. The trends in the sorption rates suggest that sorption bias would be problematic for flexible polymers and compounds with large K_{ow} (octanol-water partition coefficient) values. However, a more quantitative understanding is needed to enable sorption bias to be usefully predicted. The present studies focus on higher K_{ow} compounds and on the prediction of sampling bias when polymeric tubing is used in conjunction with a pump to convey water samples to their containers. The sorption rates were measured by batch sorption experiments, similar to those employed in the previous studies, and by inverse chromatography, in which the analytical column of a gas chromatograph was replaced by a length of polymeric tubing. The chromatographic experiments were carried out to verify a model for predicting sorption bias in polymeric transfer line tubing.

METHODS

Four materials, polyethylene, poly(tetrafluorethylene) (teflon), rigid poly(vinyl chloride) (PVC) and stainless steel, were tested in the batch sorption experiments. The latter three materials are commonly used in sampling surface and ground water for organic contaminants. Polyethylene was included to serve as a reference for comparing with literature data. The compounds included chlorobenzene (1-Ben), m-dichlorobenzene (2-Ben), 1,2,4-trichlorobenzene (3-Ben), 1,2,4,5-tetrachlorobenzene (4-Ben), hexachlorobenzene (6-Ben), 2,4-dichlorobiphenyl (2-Pcb), 2,2',5-

trichlorobiphenyl (3-Pcb), 2,2',4,4'-tetrachlorobiphenyl (4-Pcb), and 2,2',3,4,5'-pentachlorobiphenyl (5-Pcb). These compounds were chosen for the range of octanol-water partition coefficient they represent, 2.8 < log K_{ow} < 6.5, and because they are common organic contaminants. The range of log K_{ow} investigated in the previous experiments was approximately 2.1 to 3.4.

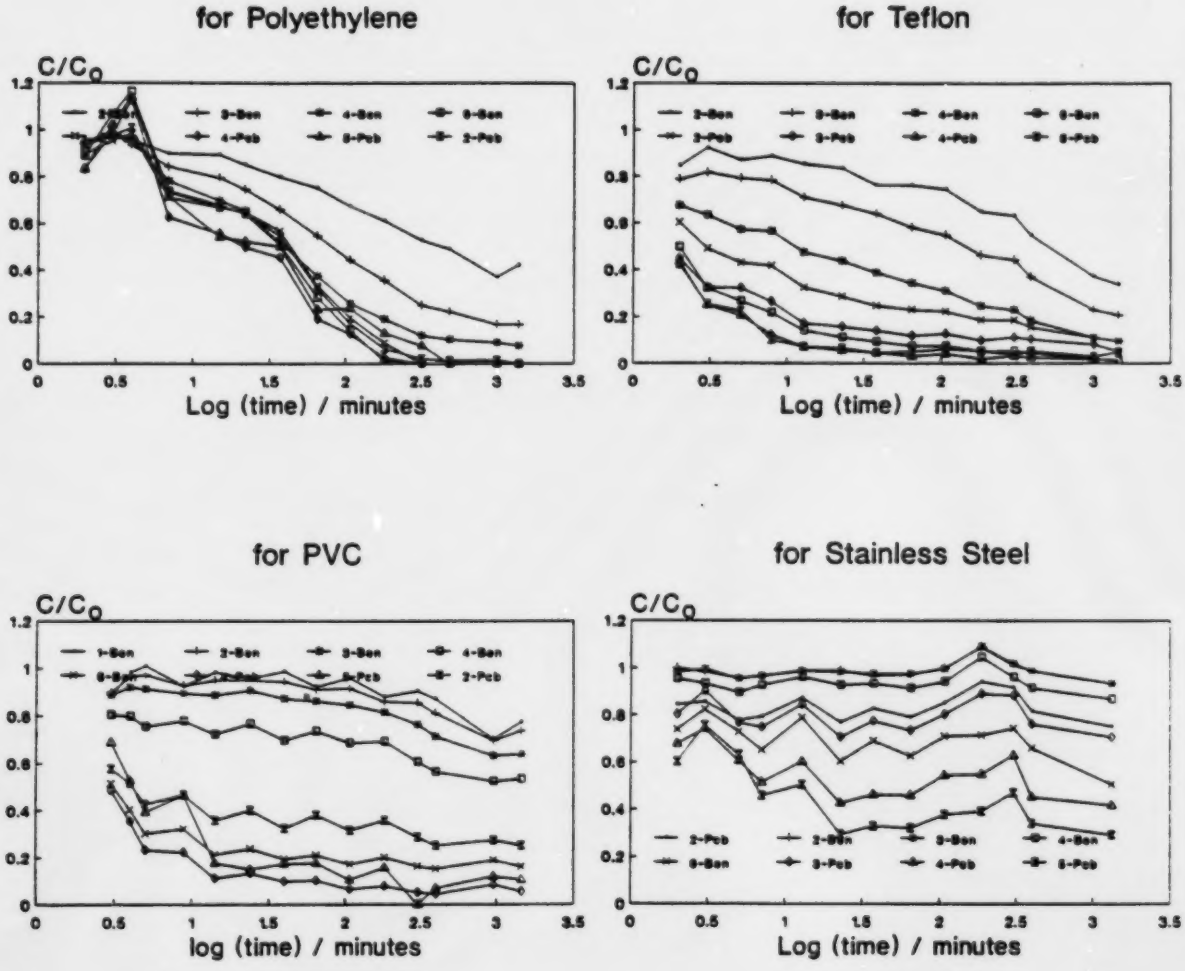
The method used for measuring the sorption rate constants is similar to that used previously (3,4). Briefly, the material was cut into small, uniform-sized pieces which were distributed equally among 160 mL glass hypovials. After weighing 100 mL aliquots of spiked water into the hypovials, they were immediately capped with teflon-faced silicone rubber septa and placed in a 400 rpm rotary shaker. Three hypovials containing the material being tested and an additional control hypovial, containing only the spiked water, were sampled at each of fourteen logarithmically-spaced sampling times. The maximum exposure time was 24 hours; in the previous experiments, maximum exposure times of 5 to 8 weeks were used. To determine the solution concentration, the material was removed from the hypovial and the water in the hypovial was extracted with 2 mL of iso-octane. An aliquot of the iso-octane was analyzed by gas chromatography using an HP 5890A with splitless injection, a 60 m x 0.32 mm, 25 um DB-5 fused silica capillary column, and an electron capture detector. To ensure that the sorption rate constants would be adequately determined for most of the compounds, the number of pieces of material placed in each hypovial was adjusted, by calculation or by trial and error, so that the compounds in the middle of the log K_{ow} range were depleted by about 50 % in 30 minutes. This resulted in solution volume to polymer surface area ratios ranging from 0.286 cm (PVC) to 9.35 cm (polyethylene); the ratio for stainless steel was 0.470 cm. The shapes of the materials varied: for teflon and PVC, 1 cm x 7 cm pieces were cut from sheet 0.159 cm stock; for polyethylene and stainless steel, 3.175 cm lengths were cut from 0.635 cm O.D. tubing. The initial concentrations of the compounds were chosen to be about 1/100 of their water solubilities to avoid non-Fickian diffusion in the polymers.

The inverse chromatography experiments were carried out with various lengths and internal diameters of teflon and polyethylene tubing installed in an HP 5890A gas chromatograph in place of the analytical column. The compounds investigated include benzene, toluene and ethyl benzene. A square pulse of organic vapour was introduced into the nitrogen carrier gas stream by means of a 25 mL sample loop installed in a gas sampling valve. The loop was constructed from 1/4 " O.D. glass tubing and 1/4 " x 1/16 " Swagelock fittings. The sample loop was filled with an organic vapour at a partial pressure of about 0.01 atm with a 50 mL glass syringe. The shapes of the frontal breakthrough curves were monitored by recording area slice files sent from an HP 3392A integrator to an IBM PC computer. The response of the flame ionization detector was calibrated by recording the area of the pulse when a 1/4 " glass column replaced the polymeric tubing.

RESULTS

Plots of relative concentration, C(t)/C(t=0), versus log(t) (minutes) for the four materials are shown in Figure 1. The sigmoid shape of the curves for the polymers is similar to that observed in the previous experiments. However, the curves for stainless steel do not appear to be sigmoid-shaped. As was observed in the previous experiments, the rate of sorption by polymers increases as the solubility of the compound in water decreases, or as the octanol-water partition coefficient increases. The data for the experiments with stainless steel also show greater losses for compounds with lower solubilities.

Figure 1. **Variation of relative concentration, C/C_o with time for the batch sorption experiments.**



Values of the sorption rate constant, K^2D (cm^2/s), were obtained by fitting the C/C_0 data to the static model by methods similar to those described previously [4]. Log K^2D is related to the time at which 50 % of the compound is lost from solution, $t_{1/2}$ (s), by the formula:

$$\log (K^2D) = - 0.233 + 2 \log a - \log (t_{1/2}) \qquad (1)$$

where a (cm) is the ratio of the solution volume to the polymer surface area. The log $t_{1/2}$ values were obtained by visually fitting theoretical curves to the experimental data. The relationship between log K^2D and the solubility of the compound in water, log C_s (mol/m^3), for the three polymers is shown in Figure 2. The data for the previous measurements are also plotted for comparison. The three sets of measurements are labelled chronologically: Series 1 refers to the low molecular weight halocarbons, Series 2 refers to the low molecular weight aromatic hydrocarbons, and Series 3 refers to the chlorobenzenes and PCB's. A linear relationship between log K^2D and log C_s is evident for the Series 3 compounds in all three polymers; the regression lines are indicated. Although an overall trend exists, the three data sets do not appear to be completely consistent; a discontinuity between the Series 3 data and the other two series is apparent. Figure 2 also shows that the sorption rate constants are considerably greater for polyethylene than for teflon or PVC.

The dynamic model selected for describing the loss of organic solutes from a fluid flowing through a polymeric tubing was adapted from a heat exchange model [5] and a model for diffusion into the rock matrix of a parallel fissure [6]. The assumptions are similar to those employed in the static model (e.g. planar geometry), and inversion of the model yields a sorption rate constant similar to that obtained for the batch sorption experiments. The model equations and their solution are given below.

Equations:

$$\partial c / \partial t = D (\partial^2 c / \partial z^2) \qquad (2)$$

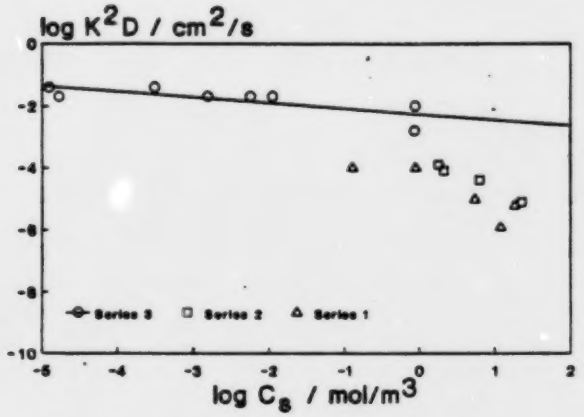
$$(a / KD) ((\partial C / \partial t) + U(\partial C / \partial x)) = (\partial c / \partial z) \qquad (3)$$

Boundary and Initial Conditions (4)

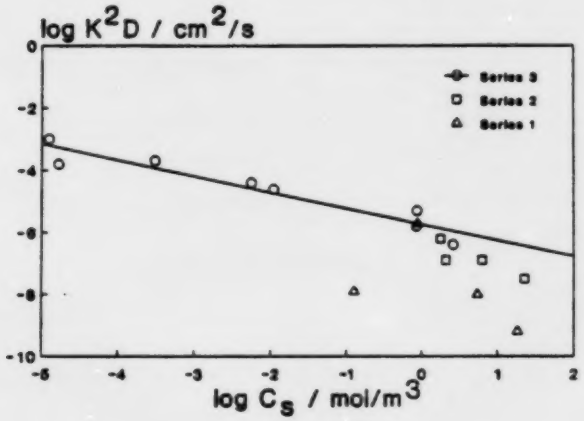
Solution:

$$C / C_0 = \text{erfc} (t_R (K^2D)^{1/2} / 2a (t - t_R)^{1/2}) \qquad (5)$$

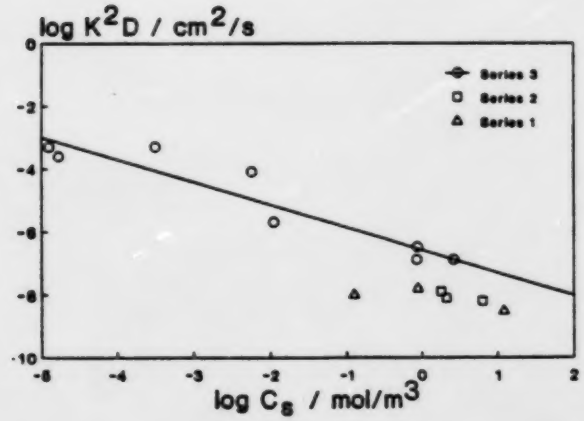
Figure 2. **Log K^2D versus log C_s plots for polyethylene, teflon, and rigid PVC. Series 1 and 2 data are for the low molecular weight halogenated and aromatic hydrocarbons, respectively. Series 3 data are for the chlorobenzenes and PCBs presently investigated. The regression lines for Series 3 data are also indicated.**



POLYETHYLENE



TEFLON



PVC

The fluid is flowing at velocity, U (cm/s), in the positive x direction between two parallel, semi-infinite polymer slabs separated by a distance 2a. The solute, at concentration, C (mol/m^3) in the fluid, diffuses perpendicularly into the slabs (z direction), at concentration, c (mol/cm^3). D (cm^2/s) is the diffusivity of the solute in the polymer, and K (dimensionless) is the polymer-water partition coefficientt (or polymer-air partition coefficient when the fluid is a gas). It is assumed that diffusion in the polymer is rate limiting and that no mixing or diffusion occurs in the direction of flow. C/C_0 is the concentration of solute in the fluid at time, t (s), and distance, x (cm), along the fissure divided by the concentration at $t = 0$, $x = 0$; t_R (s) is the residence time of the fluid in the fissure, and erfc denotes the error function complement. Some theoretical breakthrough curves are shown in Figure 3.

In preliminary gas chromatography experiments, the carrier gas flowrate was varied, several lengths and internal diameters of teflon tubing were tried, and several aromatic hydrocarbon vapours were injected. It was observed that the breakthrough curves behaved qualitatively in the manner predicted by the model. The curves flattened when the flowrate decreased, the tubing length increased, the tubing diameter decreased, and the boiling temperature of the compound increased. It was also observed that the shapes of the breakthrough curves were adequately described by the model; a representative parity plot is shown in Figure 4. K^2D values were obtained by visually comparing the experimental breakthrough curves with a series of calculated curves differing by 0.1 units in log K^2D. The K^2D (polymer-air) values were converted to K^2D (polymer-water) values by means of the dimensionless Henry's law constant for partitioning in water [7]. The correspondence between the the log K^2D values obtained from the GC experiments and those obtained by batch sorption experiments is shown in Table 1.

Table 1. **A comparison of log K^2D (cm^2/s) values obtained by the GC experiments and those obtained by the batch sorption experiments.**

Polymer/Compound	Method	
	Inverse GC	Batch Sorption
polyethylene/benzene	-5.2	-5.1
teflon/benzene	-7.2	-7.5
teflon/toluene	-6.3	-6.9
teflon/ethyl benzene	-5.9	-6.5

Figure 3. **Breakthrough curves calculated by eq. 5 for various values of log K^2D with t_R = 29.7 s and a = 0.0794 cm.**

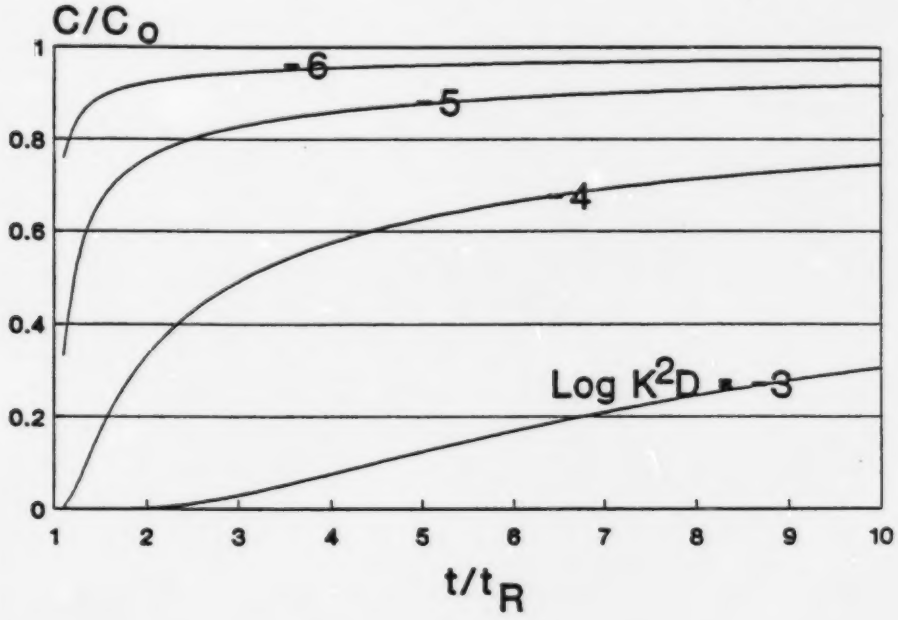
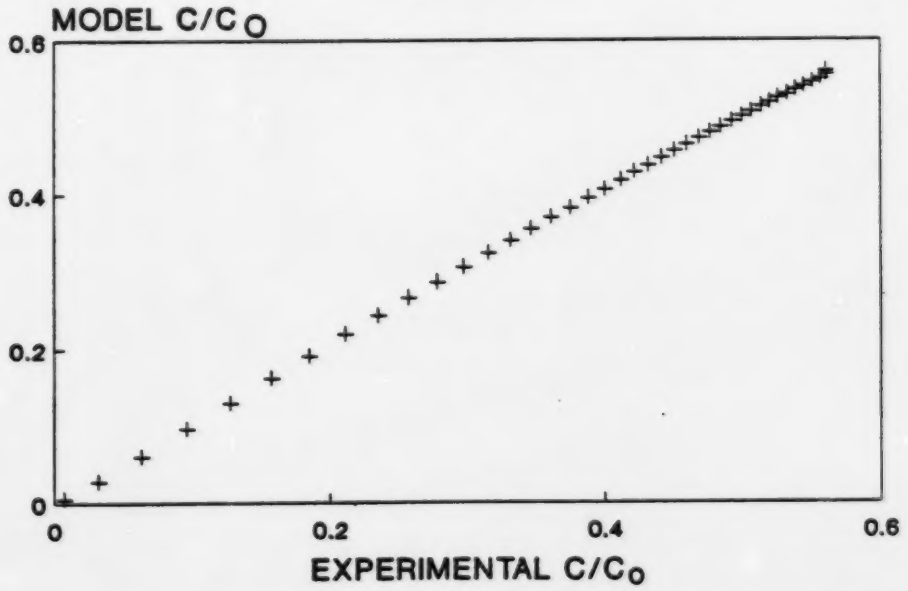


Figure 4. **Parity plot for a breakthrough curve for ethylbenzene vapour in a 1/16" I. D. teflon tubing.**



DISCUSSION

Several difficulties were encountered in measuring the log K^2D values for chlorobenzenes and PCB's in the polymers by batch sorption experiments. Because the chlorobenzenes and PCB's were much more rapidly absorbed than the previously studied compounds, it was necessary to reduce the exposure period and increase the sampling frequency accordingly. The first few hypovials were sampled within a period of five minutes. In the case of polyethylene, it was also necessary to increase the solution volume to polymer surface area ratio, a, to about 9 from the previous 0.3 cm. In the previous experiments, a tipping shaker was used at 2 cycles/minute. whereas in the present experiments the hypovials were shaken much more vigorously (400 rpm on a rotary shaker). In comparing the two methods of shaking, it was observed that the log K^2D values for the series 3 compounds in polyethylene were on average about one order of magnitude larger when the hypovials were shaken vigorously, implying that diffusion in the liquid phase contributes significantly to the overall mass transfer resistance. The diffusion model that was used to interpret the results, however, does not take this into account. Some bias may therefore exist in the measured log K^2D values. The bias should be largest for compounds having the largest K_{ow} values. This fact and the previously found consistency between the literature and the experimentally determined values for K and D [4] suggests that the bias is not severe for the Series 1 and 2 compounds. Mass transfer resistance in the liquid phase may be responsible for the discontinuity between the Series 3 and the Series 1 and 2 data sets seen in Figure 2. It may also be responsible for the poorly resolved sorption curves (C/C_0 vs log t) for the higher K_{ow} compounds in polyethylene (Figure 1).

The evidence supporting the diffusion model interpretation of the batch sorption experiments for the low molecular weight halogenated and aromatic hydrocarbons has been previously discussed [4]. The sorption curves for the chlorobenzenes and PCB's generally conform to the shape predicted by the diffusion model. However, due to the very wide range of water solubilities represented by the experimental compounds, many of the sorption curves are not well determined experimentally, i.e. only the beginning or the ending portions are determined. In preliminary experiments with teflon, the value of a was varied between 2.4 and 0.24 while the maximum exposure time was kept constant at 24 hours; the resulting values of log K^2D were self-consistent. The approximate solution to the differential equations for sorption that was utilized to calculate the log K^2D values [4] is based on the assumption that the equilibrium concentration is small relative to the initial concentration. The curves should thus be superimposable when shifted on the log t axis. The apparent lack of superimposability of the curves for polyethylene and for PVC may be due to the fact that some of the curves apparently attain non-zero equilibrium C/C_0 values. The existence of linear relationships between log K^2D and log C_s for the chlorobenzenes and PCB's in the three polymers (Figure 2) is consistent with the diffusion model and with the trends in the Series 1 and 2 data [4]. For example, when log K and log D for the chlorobenzenes and PCB's in polyethylene are estimated from the boiling tempertures and molar volumes using the empirical relationships derived from the Series 1 and 2 data, the resulting log K^2D values are generally within 0.4 units of the experimentally determined ones. The linear relationships can be used to predict log K^2D values for previously unmeasured compounds.

The appropriateness of the model used in this study to describe the effects of sorption on the concentration of a vapour moving through a polymeric tubing is supported by the following observations: the response of the breakthrough curve to changes in compound and polymer identity, tubing length and diameter, and carrier gas velocity was correctly predicted; the shape of the

breakthrough curve was adequately described; limited agreement was observed between K^2D values obtained from several GC experiments and those obtained from the batch sorption experiments. The K^2D value for ethyl benzene obtained from the GC method was appreciably larger than that from the batch sorption experiment (Table 1). The reason for this discrepancy is not known, but it may be related to the fact that the shape of the square pulse was distorted for the higher boiling temperature compounds relative to the lower when the polymer tubing was replaced by glass for calibration purposes. An expanded effort would be required to fully evaluate the inverse chromatography technique for determining values of K^2D. Further studies should include using a liquid chromatograph in conjunction with a gas chromatograph to test the assumption that mass transfer resistance in the fluid phase can be neglected. However, the present evidence provides justification for applying the dynamic model to predict the effects of sorption on the concentration of trace organic compounds in water sampled with a length of polymeric tubing.

It was shown in a previous paper [3] that the static sorption model can be used to predict the maximum time that a sample should be exposed to the well material, i.e. the time interval between purging and sampling the well, based on the assumption that a 10 % sampling error is the largest that can be tolerated. In a typical monitoring situation, the well is 1 inch in diameter, is constructed of rigid PVC, and the compounds being determined have water solubilities greater than 0.1 mol/m^3 (e.g. low molecular weight halogenated or aromatic hydrocarbons). The maximum exposure time for this situation is about 10 hours. Occasionally however, compounds having considerably lower solubilities are determined; the compounds used in the present study for example have log C_s values as small as -5. The maximum exposure time for this situation is 3.8 seconds, a difficult requirement to satisfy. Similar predictions can be made for sampling surface water with a grab sampler. For example, if a 5 L PVC Niskin bottle is used to sample the chlorobenzenes and PCB's, the maximum exposure time, i.e. the time interval between capturing the sample and removing it from the Niskin, is 84 seconds. The following assumptions have been made in applying the static sorption model to predict maximum exposure times: the water in the well does not exchange with that outside after the well is purged; the water in the well or grab sampler is well mixed; there is no prior exposure of the polymer to the water containing the compounds being determined. If any of the assumptions are not realized, the maximum exposure time will be over-estimated. Note that the static model is not appropriate for predicting leaching or desorption of compounds from the polymer into the water sample. Also, the assumption of planar geometry leads to some ambiguity when applying the model to cylinders; here, as in the batch sorption experiments, the parameter, a, has been taken as the water volume to polymer surface area ratio, which is equal to 1/2 the radius of the cylinder.

Can sampling tubing be equilibrated with the water to be sampled, thus negating this sorption sampling bias? The same kind of reasoning can be applied to predicting the minimum flushing time required to obtain a sufficiently representative sample of water flowing from a polymer transfer line tubing. Figure 3 shows the results of a simulation for a typical application for a common groundwater sampling system which is often used in research, the Waterloo multilevel piezometer system). Here, water flows through a 5 m length of 1/16 " ID teflon tubing at 20 mL/min; the residence time of the water in the tubing, t_R, is approximately 30 seconds. It is obvious from the figure that as the value of log K^2D increases from - 6 to -3, the breakthrough curve flattens dramatically. For convenience, the minimum flushing time can be defined as the time required for C/C_0 to attain an instantaneous value of 0.9. This criterion ensures that the solute concentration in a finite sample will be at least 90 % of C_0. Figure 2 shows a maximum value of -3 for log K^2D. Inverting eq 5 for $C/C_0 = 0.9$ then yields a value for t of 5 hr. This calculation suggests that it may be impractical to use a small diameter teflon tubing to sample very hydrophobic organic compounds.

Another typical situation would be a 5 m length of 1/2 " ID polyethylene tubing and a flowrate of 5 L/min (e.g. the WaTerra sampler). Figure 2 indicates a maximum value of -1 for log K^2D, and eq 5 indicates a minimum flushing time of 30 minutes. This is probably a longer time period than would normally be allowed. If mass transfer resistance in the liquid phase is important, the minimum flushing times will be over-estimated. These calculations suggest that sorption can be problematic for sampling moderately hydrophobic organic compounds with systems utilizing small diameter plastic tubing if insufficient attention is given to allowing adequate flushing times for equilibrating the transfer line tubing with the water sample.

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